

What is claimed is:

1. A gas-permeable membrane which comprises
  - (a) a microporous polymeric film, and
  - (b) a polymeric coating on the microporous film, the polymeric coating changing the permeability of the microporous film so that the membrane
    - (i) has a  $P_{10}$  ratio, over at least one 10°C range between -5 and 15°C, of at least 1.3;
    - (ii) has an oxygen permeability (OTR), at all temperatures between 20° and 25°C, of at least 775,000 ml/m<sup>2</sup>.atm.24 hrs (50,000 cc/100 inch<sup>2</sup>.atm.24 hrs; and
    - (iii) has a CO<sub>2</sub>/O<sub>2</sub> permeability ratio(R) of at least 1.5;the  $P_{10}$ , OTR and R values being measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi)
- 15 2. A membrane according to claim 1 which has at least one of the following characteristics
  - (1) the microporous film has an average pore size of less than 0.24 micron;
  - (2) the microporous film has a tear strength of at least 30g;
  - (3) the microporous film has a Sheffield Smoothness of at least 30;
  - 20 (4) the microporous film comprises a polymeric matrix comprising an essentially linear ultrahigh molecular weight polyethylene having an intrinsic viscosity of at least 18 deciliters/g;
  - (5) the microporous film comprises a polymeric matrix comprising an essentially linear ultrahigh molecular weight polypropylene having an intrinsic viscosity of at least 6 deciliters/g;
  - 25 (6) the microporous film comprises a finely divided, particulate, substantially insoluble filler which is distributed throughout the film;
  - (7) the coating weight of the coating polymer is 1.7 to 2.9 g/m<sup>2</sup>; and
  - (8) the coating polymer is a crystalline polymer having a  $T_p$  of -5° to 15°C.

3. A membrane according to claim 1 which has a  $P_{10}$  ratio between 0 and 10°C of at least 2.6, the  $P_{10}$  being measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi).

4. A membrane according to claim 2 which has a  $P_{10}$  ratio between 0 and 10°C of at least 2.6, the  $P_{10}$  being measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi).

5. A membrane according to claim 1 which has a  $P_{10}$  ratio, over at least one 10°C range between -5°C and 15°C, of at least 2.6, an OTR at all temperatures between 20°C and 25°C of at least 1,550,000 ml/m<sup>2</sup>.atm.24 hrs (100,000 cc/inch<sup>2</sup>.atm.24 hrs, and an R ratio of at least 2.5, the  $P_{10}$ , OTR and R values being measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi).

5. A membrane according to claim 2 which has a  $P_{10}$  ratio, over at least one 10°C range between -5°C and 15°C, of at least 2.6, an OTR at all temperatures between 20°C and 25°C of at least 1,550,000 ml/m<sup>2</sup>.atm.24 hrs (100,000 cc/inch<sup>2</sup>.atm.24 hrs, and an R ratio of at least 2.5, the  $P_{10}$ , OTR and R values being measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi).

7. A membrane according to claim 1 wherein at least 90% of the pores have a pore size less than 0.24 micron, and which has a  $P_{10}$  ratio, over at least one 10°C range between -5 and 15°C of at least 1.3, an OTR of 775,000 to 3,100,000 ml/m<sup>2</sup> atm.24 hrs (50,000 to 200,000 cc/100 inch<sup>2</sup>.atm 24 hrs), and an R ratio of at least 2, the  $P_{10}$ , OTR and R values being measured at a pressure of 0.7 kg/cm<sup>2</sup> (10 psi).

25 8. A membrane according to claim 7 which has at least one of the following characteristics

(1) it has a  $P_{10}$  ratio of at least 1.3 over at least one 10°C temperature range between 0° and 15°C;

(2) it has a  $P_{10}$  ratio of at least 2 over at least one 10°C temperature range between 0° and 15°C;

(3) it has a  $P_{10}$  ratio of at least 2.5 over at least one 10°C temperature range between 0° and 15°C;

(4) it has an OTR of at least 1,550,000 ml/m<sup>2</sup>.atm.24 hrs (100,000 cc/100 inch<sup>2</sup>.atm.24 hrs);

5 (5) it has an OTR of at least 2,325,000 ml/m<sup>2</sup>.atm.24 hrs (150,000 cc/100 inch<sup>2</sup>.atm.24 hrs);

(6) it has an OTR of 775,000 to 3,100,000 ml/m<sup>2</sup>.atm.24 hrs (50,000 to 10 200,000 cc/100 inch<sup>2</sup>.atm.24 hrs) and an R value of more than (3.8 - 0.00000045P), where P is the OTR in ml/m<sup>2</sup>.atm.24 hrs;

(7) it has an OTR of 775,000 to 3,100,000 ml/m<sup>2</sup>.atm.24 hrs (50,000 to 10 200,000 cc/100 inch<sup>2</sup>.atm.24 hrs) and an R value of (3.8 - 0.00000045P) to (7.4 - 0.000016P), where P is the OTR in ml/m<sup>2</sup>.atm.24 hrs;

(8) it has an OTR of 775,000 to 3,100,000 ml/m<sup>2</sup>.atm.24 hrs (50,000 to 15 200,000 cc/100 inch<sup>2</sup>.atm.24 hrs) and an R value of (3.8 - 0.00000045P) to (5.6 - 0.000084P), where P is the OTR in ml/m<sup>2</sup>.atm.24 hrs;

(9) it has an R ratio of at least 2.5; and

(10) it has an R ratio of at least 3.

the  $P_{10}$ , OTR and R values being measured at a pressure of 0.07 kg/cm<sup>2</sup> (10 psi).

20 9. A membrane according to claim 7 wherein the microporous film has at least one of the following characteristics:

(1) substantially 100% of the pores have a pore size less than 0.24 micron;

(2) at least 80% of the pores have a pore size less than 0.15 micron;

(3) at least 70% of the pores have a pore size less than 0.11 micron;

25 (4) the pores constitute 35 to 80% of the volume of the film;

(5) the pores constitute 60 to 75% of the volume of the film;

(6) it comprises a polymeric matrix composed of

30 (a) essentially linear ultrahigh molecular weight polyethylene having an intrinsic viscosity of at least 18 deciliters/g, or

(b) essentially linear ultrahigh molecular weight polypropylene having an intrinsic viscosity of at least 6 deciliters/g, or

- (c) a mixture of (a) and (b);
- (7) it comprises (i) a polymeric matrix, and (ii) 50 to 90% by weight, based on the weight of the microporous film, of a finely divided, particulate, substantially water-insoluble, siliceous filler which is distributed throughout the matrix; and
- (8) it has been calendered at a nip pressure of 17.8 to 266.6 kg/linear cm (100 to 1,500 pli) before or after the coating is formed thereon.

10. A membrane according to claim 8 wherein the microporous film has at least one of the following characteristics:

- (1) substantially 100% of the pores have a pore size less than 0.24 micron;
- (2) at least 80% of the pores have a pore size less than 0.15 micron;
- (3) at least 70% of the pores have a pore size less than 0.11 micron;
- (4) the pores constitute 35 to 80% of the volume of the film;
- (5) the pores constitute 60 to 75% of the volume of the film;
- (6) it comprises a polymeric matrix composed of
  - (a) essentially linear ultrahigh molecular weight polyethylene having an intrinsic viscosity of at least 18 deciliters/g, or
  - (b) essentially linear ultrahigh molecular weight polypropylene having an intrinsic viscosity of at least 6 deciliters/g, or
  - (c) a mixture of (a) and (b);
- (7) it comprises (i) a polymeric matrix, and (ii) 50 to 90% by weight, based on the weight of the microporous film, of a finely divided, particulate, substantially water-insoluble, siliceous filler which is distributed throughout the matrix; and
- (8) it has been calendered at a nip pressure of 17.8 to 266.6 kg/linear cm (100 to 1,500 pli) before or after the coating is formed thereon.

11. A membrane according to claim 7 wherein the coating polymer has at least one of the following characteristics:

(1) it is a crystalline polymer having a  $T_p$  of -5 to 40°C and a  $\Delta H$  of at least 5 J/g;

(2) it is a crystalline polymer having a  $T_p$  of 0 to 15°C and a  $\Delta H$  of at least 20 J/g;

5 (3) it is a side chain crystalline polymer;

(4) it is a side chain crystalline polymer in which  $T_p-T_o$  is less than 10°C;

(5) it is a side chain crystalline polymer prepared by copolymerizing (i) at least one n-alkyl acrylate or methacrylate in which the n-alkyl group contains at least 12 carbon atoms and (ii) one or more comonomers selected from acrylic acid, methacrylic acid, and esters of acrylic or methacrylic acid in which the esterifying group contains less than 10 carbon atoms;

10 (6) it is cis-polybutadiene, poly(4-methylpentene), polydimethyl siloxane, or ethylene-propylene rubber; and

15 (7) it has been crosslinked.

12. A membrane according to claim 8 wherein the coating polymer has at least one of the following characteristics:

(1) it is a crystalline polymer having a  $T_p$  of -5 to 40°C and a  $\Delta H$  of at least 5 J/g;

20 (2) it is a crystalline polymer having a  $T_p$  of 0 to 15°C and a  $\Delta H$  of at least 20 J/g;

(3) it is a side chain crystalline polymer;

(4) it is a side chain crystalline polymer in which  $T_p-T_o$  is less than 10°C;

25 (5) it is a side chain crystalline polymer prepared by copolymerizing (i) at least one n-alkyl acrylate or methacrylate in which the n-alkyl group contains at least 12 carbon atoms and (ii) one or more comonomers selected from acrylic acid, methacrylic acid, and esters of acrylic or methacrylic acid in which the esterifying group contains less than 10 carbon atoms;

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- (6) it is cis-polybutadiene, poly(4-methylpentene), polydimethyl siloxane, or ethylene-propylene rubber; and
- (7) it has been crosslinked.

5 13. A membrane according to claim 9 wherein the coating polymer has at least one of the following characteristics:

- (1) it is a crystalline polymer having a  $T_p$  of -5 to 40°C and a  $\Delta H$  of at least 5 J/g;
- (2) it is a crystalline polymer having a  $T_p$  of 0 to 15°C and a  $\Delta H$  of at least 20 J/g;
- (3) it is a side chain crystalline polymer;
- (4) it is a side chain crystalline polymer in which  $T_p - T_o$  is less than 10°C;
- (5) it is a side chain crystalline polymer prepared by copolymerizing (i) at least one n-alkyl acrylate or methacrylate in which the n-alkyl group contains at least 12 carbon atoms and (ii) one or more comonomers selected from acrylic acid, methacrylic acid, and esters of acrylic or methacrylic acid in which the esterifying group contains less than 10 carbon atoms;
- (6) it is cis-polybutadiene, poly(4-methylpentene), polydimethyl siloxane, or ethylene-propylene rubber; and
- (7) it has been crosslinked.

14. A membrane according to claim 1 wherein the coating polymer has at least one of the following characteristics:

- (1) it is an acrylate polymer containing at least 40% by weight of units derived from a cycloalkyl acrylate or methacrylate;
- (2) it is a fluoropolymer;
- (3) it is an acrylate polymer containing units derived from a fluoroalkyl acrylate or methacrylate;
- (4) it is an acrylate polymer containing 10 to 70% of units derived from a polyethylene glycol acrylate or methacrylate.

15. A membrane according to claim 1 wherein the microporous polymeric film contains pores which are partially blocked by a polymer having an R ratio of less than 1.3 or by a particulate material, or (b) has an OTR before coating of less than 15,500,000  
5 (1,000,000).

16. A package which is stored in air and which comprises  
(a) a sealed container, and  
(b) within the sealed container, a respiring biological material and a packaging atmosphere around the biological material  
10 the sealed container including one or more permeable control sections which provide substantially the only pathways for oxygen and carbon dioxide to enter or leave the packaging atmosphere, at least one said permeable control section being a gas-permeable membrane as defined in claim 1.

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17. A package according to claim 16 wherein the control section is in the form of a strip which extends across a complete dimension of the container.

18. A package which is stored in air and which comprises  
20 (a) a sealed container, and  
(b) within the sealed container, a respiring biological material and a packaging atmosphere around the biological material  
the sealed container including one or more permeable control sections which provide substantially the only pathways for oxygen and carbon dioxide to enter or leave the  
25 packaging atmosphere, at least one said permeable control section being a gas-permeable membrane as claimed in claim 7.

19. A package which is stored in air and which comprises  
30 (a) a sealed container, and  
(b) within the sealed container, a respiring biological material and a packaging atmosphere around the biological material

the sealed container including one or more permeable control sections which provide substantially the only pathways for oxygen and carbon dioxide to enter or leave the packaging atmosphere, at least one said permeable control section being a gas-permeable membrane as claimed in claim 14.